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11152Thermodynamics of metallocene catalyst
activation: alignment of theory and experiment†Mikko Linnolahti * and Scott Collins ‡

Three equilibria involved in metallocene catalyst activation, including dissociation of R_2Al_2 ($R = Me, Et$ or $i-Bu$) and related species such as $[L_2ZrMe_2AlMe_2][B(C_6F_5)_4]$ ($L_2 = Cp_2, 1,2$ -ethylenebis(η^5 -indenyl)), $Me_2C(\eta^5-C_5H_4)_2$ or $[(L_2ZrMe)_2\mu-Me][MePBB]$ ($L_2 = (h^5-1,2-Me_2C_5H_3)_2$, $[MePBB]^- = [MeB(Ar_F)_3]^-$ with $Ar_F = o-C_6F_5-C_6F_4$) are studied by DFT using various approaches to account for the enthalpy and entropy changes in gas and condensed phases. These studies reveal that both low energy vibrations and translational entropy conspire to cause significant deviations between theory and experiment when it comes to the free energy change in condensed or even gas phase. Alignment of theory with experiment requires in addition, consideration of specific solvation of reactants and products.

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Introduction

Over the past several years there has been renewed study of the structure and reactivity of large aluminosilicate structures with formulae $(MeAlO)_n (Me_3Al)_m$.¹ These are thought to be models for methylaluminosilicate (MAO), and in particular for the active components of that mixture, as MAO is commonly used to activate group 4 metallocene and other single site catalysts for olefin polymerization.²

Previous computational studies have focused on systematic evaluation of the structure of MAO,³ including following its formation *via* hydrolysis of Me_3Al .⁴ The growth of MAO oligomers has been demonstrated to start out as linear aggregates, rings and sheet structures with tetrahedral Al and trigonal O.⁵ Hydrolysis studies of the initial steps have employed MP2 level of theory, while in subsequent work, approaching the experimentally relevant size-domain,⁶ we adopted the more cost-effective M06-2X DFT method,⁷ combined with a basis set of triple zeta quality,⁸ since this functional is well known to treat dispersion forces in the $Al-\mu-Me-Al$ or $(\mu^4-O)Al_4$ bonding found in the structures.⁹

Transition from sheets to cages was initially proposed at *ca.* $n \sim 13$, and a stable cage was located with $n = 16$ and $m = 6$,⁶ which corresponds to the composition of the most intense anion detected by ESI MS upon reaction of hydrolytic MAO with Lewis bases, including metallocene complexes.¹⁰

However, some of the Me_3Al was incorporated as structural $Me_3Al^{1d,e,11}$ – *i.e.* as linear but aggregated $Me_2Al(OAlMe)_xMe$ moieties in this unstrained cage rather than terminal OAl_2Me_5 groups. Based on the number of readily exchangeable Al-Me groups as detected using *e.g.* Et_3Al and ESI-MS,¹² the cage structure did not seem reasonable. This guided us toward a more detailed investigation of the structural motifs, revealing that transition from sheets to cages does not take place at $n \leq 18$. The reason for the preference of sheets over isomeric cages lies in significantly higher entropy, and hence lower free energy, of the sheets. An especially stable sheet anion $[(MeAlO)_{16}(Me_3Al)_6Me]^-$ (hereinafter **[16,6]**[−]) along with its neutral **16,6** precursor does possess the requisite number of exchangeable Al-Me groups.¹³

Accurate calculation of entropy, and thus free energy, requires special attention. As systems get large, the number of low energy normal modes increase dramatically and to the point where it is difficult to estimate their energy, and thus the vibrational entropy using a harmonic oscillator approximation. This is a general and well-known problem, for which quasi-harmonic entropy corrections have been proposed, *e.g.* by raising the problematic low energy vibrations to a cut-off frequency of 100 cm^{-1} .¹⁴

We noticed the importance of this particularly for isomeric structures differing little in the arrangement of the constituent atoms (*i.e.*, conformers) as in recently proposed contact ion-pairs (CIP) between Cp_2ZrMe_2 and our new sheet model for **16,6** (Fig. 1).¹⁵

The calculated TS values of these isomers had a variation of $\sigma = \pm 6.1\text{ kJ mol}^{-1}$ at 298 K. Though the standard deviation is small compared with the total entropy for these large systems (*ca.* 0.75%), in free energy terms this corresponds to a significant amount and might overwhelm attempts to characterize

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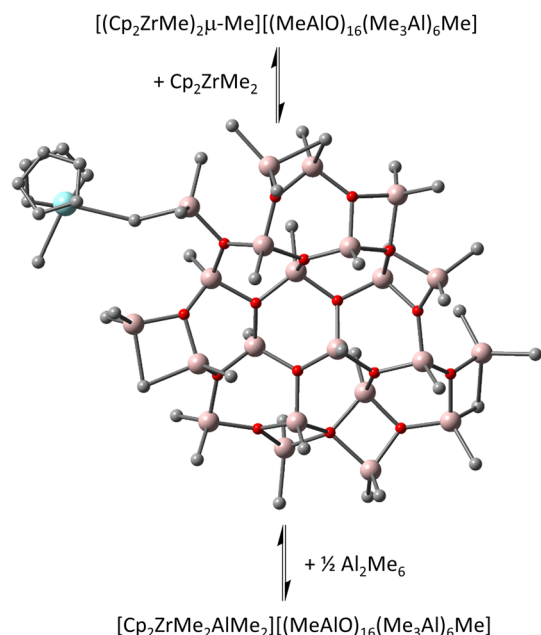


Fig. 1 Equilibria involving contact ion-pair to form outer-sphere ion-pairs detected spectroscopically.¹⁵ Zr in blue, Al in pink, O in red, C in grey, H omitted for clarity.

the reactivity of these large structures in gas phase but also importantly in solution. For example, outer-sphere ion-pairs (OSIP) that have been detected spectroscopically in the case of the Cp_2ZrMe_2 -MAO system include $[\text{Cp}_2\text{ZrMe}_2\text{AlMe}_2][\mathbf{16,6}]$ and $[(\text{Cp}_2\text{ZrMe})_2\mu\text{-Me}][\mathbf{16,6}]$ ¹⁵ and yet the equilibria between these species and any contact ion-pairs present are not as well-documented, in contrast to other ion-pairs featuring well-defined counter-anions.²

Accurate computation of thermodynamic quantities in solution is a topic of great difficulty and debate – we cannot provide here an in-depth discussion but refer the reader to recent literature.¹⁶ We begin by noting that movements become more restricted when moving from gas-phase to solution, thereby reducing the total entropy. Hence, an approximate estimate for the solution Gibbs energy can be obtained by simply scaling the gas-phase entropy, where a $\frac{2}{3}TS$ scaling factor has been previously employed in the context of metallocenium ion-pair complexes.¹⁷ A more accurate description of specific solvents effects can be obtained by using quantum mechanical continuum solvation models,¹⁸ although these generally do not account for specific solvation of reactants *vs.* products nor effects arising from solvation such as perturbation to the thermodynamically most stable gas phase conformation. Furthermore, the continuum models do not generally account for the restricted movements in solution, and hence the entropies determined in continuum need to be further corrected, particularly for the sake of proper estimation of translational entropy.¹⁹

This prompted us to investigate this issue in more detail and for relevant catalyst activation or other reactions for which thermodynamic data was available, ideally in both gas and

condensed phases. In this paper, we discuss three different reversible reactions involving both neutral species and metallocenium ion-pairs that have been studied experimentally.

Results and discussion

Dissociation of R_6Al_2

The first equilibrium involving dissociation of R_6Al_2 ($\text{R} = \text{Me}$, Et or $i\text{-Bu}$) in gas or condensed phases has been studied in detail.²⁰ For $\text{R} = \text{Me}$, there is general agreement as to the energetics of this process in gas phase with $\Delta H = 84.2$ to 85.4 kJ mol^{-1} , $\Delta S = 177(2)$ $\text{J mol}^{-1} \text{K}^{-1}$ and $\Delta G = 31.6(0.3)$ kJ mol^{-1} at 298 K (Table 1, entries 1 and 2).²¹ The enthalpy change is accurately estimated at the M06-2X/TZVP level of theory with $\Delta H = 84.9$ kJ mol^{-1} . In the case of entropy, consideration of symmetry is required for technical correctness, because of its effect on rotational entropy.^{9,22} However, constraining Me_3Al to C_{3h} -symmetry increases the gas-phase ΔS from 244 to 282 $\text{J mol}^{-1} \text{K}^{-1}$.

The calculated reaction entropy is thus significantly larger than measured, and even more so in C_{3h} -symmetry. The origin of the increase lies in the low energy normal modes, which gain significant population at $T = 298$ K.

While the rotational entropy of Me_3Al decreases, as it should, on constraining to C_{3h} (108.9 to 99.7 $\text{J mol}^{-1} \text{K}^{-1}$), it is over-compensated by an increase in vibrational entropy (112.6 to 141.0 $\text{J mol}^{-1} \text{K}^{-1}$) due to minute changes in low energy normal modes, which cannot be calculated to precision using a harmonic oscillator approximation.

We tested Truhlar's quasi-harmonic (qh) entropy correction¹⁴ as a potential remedy for this problem, using a cut-off frequency of 100 cm^{-1} . The correction has a marked effect, reducing the reaction entropy from $\Delta S = 282$ $\text{J mol}^{-1} \text{K}^{-1}$ to $\Delta S\text{-qh} = 188$ $\text{J mol}^{-1} \text{K}^{-1}$, thus bringing it close to the experimental value of 177 $\text{J mol}^{-1} \text{K}^{-1}$.

The low energy modes also influence the zero-point correction to the electronic energy. Using a similar correction,²³ $\Delta H = 84.9$ kJ mol^{-1} reduces to $\Delta H\text{-qh} = 82.7$ kJ mol^{-1} , indicating that the M06-2X/TZVP level of theory underestimates ΔH by 2–3 kJ mol^{-1} . Thus, our best estimate for the free energy change in gas phase is $\Delta G\text{-qh} = 26.7$ kJ mol^{-1} at 298 K which is within 5 kJ mol^{-1} of the experimental value extrapolated from studies at higher T . For greater certainty we estimated $\Delta G\text{-qh}$ at 418 K in the range covered by experiment, and reasonable agreement is observed (Table 1, entry 6 *vs.* entry 3).

For $\text{R} = \text{Et}$, the dissociation equilibrium has been studied in condensed phase by several techniques (*vide infra*), though some data obtained in gas phase reported in a thesis²⁴ were disseminated in a paper by Smith.²⁵ A plot of $\ln K_d$ *vs.* $1/T$ was non-linear for Et_3Al over the temperature range studied, consistent with decomposition at higher temperatures. Thus, gas phase values of ΔH and ΔS over the T range studied are not available. At the lowest T examined (418 K) $\Delta G = 1.3(2)$ kJ mol^{-1} with estimates of $\Delta H = 76(1)$ kJ mol^{-1} and $\Delta S = 190(3)$ $\text{J mol}^{-1} \text{K}^{-1}$ based on studies of the liquid phase (*vide infra*).



Table 1 Experiment vs. theory for dissociation of R_6Al_2 in gas phase^a

Entry	R	<i>T</i> (K)	ΔH	ΔS	ΔG	ΔH -qh ^b	ΔS -qh ^b	ΔG -qh ^b	Ref.
1	Me	298	85(1)	—	—	—	—	—	21a
2	Me	298	84.2(7)	177(2)	31.6(3)	—	—	—	21b
3	Me	418	84.2(7)	177(2)	10.4(1)	—	—	—	21b
4	Et	418	76(1)	190(3)	1.3(2)	—	—	—	25
5	Me	298	84.9	282.5	0.6	82.7	187.8	26.7	This work
6	Me	418	83.5	278.7	−33.0	80.3	183.8	3.4	This work
7	Et	418	87.8	231.1	−8.8	86.0	203.6	0.8	This work

^a ΔG and ΔH in kJ mol^{-1} , ΔS in $\text{J mol}^{-1} \text{K}^{-1}$ with estimated standard deviation in parentheses for experimental data (entries 1–4). ^b Corrected for low energy vibrations using a quasi-harmonic approach.

We calculated using the quasi-harmonic correction for both H and S that ΔG -qh = 0.8 kJ mol^{-1} , which is in almost precise, though probably fortuitous agreement with the experimental value, as indicated by the larger deviations from experiment for ΔH -qh = 86.0 kJ mol^{-1} and ΔS -qh = $203.6 \text{ J mol}^{-1} \text{K}^{-1}$ at 418 K (Table 1, entries 7 vs. 4).

However, the experimental estimates are not based on the T dependence of K_d so we cannot attach too much significance to these discrepancies, except to state that we did not consider more than one conformer when calculating thermodynamic properties.²⁶

In condensed phase, experimental thermodynamic data for dissociation of liquid R_6Al_2 and solutions in aromatic or aliphatic hydrocarbons differ significantly (Table 2). Beginning with $^i\text{Bu}_3\text{Al}$, it is widely known that this compound is appreciably dissociated in condensed phase, and the accepted values in the liquid phase or hydrocarbon solution are reported in Table 2, entry 1.²⁷

The situation with Et_3Al is complicated by the technique used to determine the dissociation constants, and the temperature range over which the data was collected. The most widely cited values were reported by Smith in papers where calorimetry was used to measure the heat of dilution of this material in both hydrocarbon²⁵ and aromatic hydrocarbon²⁸ solution over a wide temperature range. His data are summarized in entries 2 and 3 where the enthalpy of dissociation is significantly lower in aromatic vs. saturated hydrocarbon media. Later work by Černý and co-workers utilized ^{27}Al NMR

spectroscopy to study this equilibrium.²⁹ Despite collecting data over a similar temperature range (25–100 °C) these workers only analyzed their data between 60–100 °C. Their estimates of ΔG based on this data (entries 4 and 5) differ significantly from those reported by Smith.

Finally, the situation for Me_3Al in condensed phase is the most confusing. Černý and co-workers also studied this equilibrium using ^{27}Al NMR spectroscopy.^{29b} The quality of the data, particularly in mesitylene solution, is not as high as that reported for Et_3Al and moreover these authors concluded that there was little difference in either the enthalpy or entropy of dissociation in comparing aromatic vs. saturated hydrocarbon solution, despite the fact that Et_3Al is more dissociated under the former conditions with a significant difference in ΔG at 298 K according to Smith.

In earlier work, Smith could not use calorimetry to study this equilibrium as Me_3Al is less dissociated than Et_3Al under all conditions.²⁵ He provided estimates based on a number of reasonable assumptions but none of the estimates are based on actual measurement of the equilibrium in question. The available data are summarized in Table 2, entries 6–9.

If we focus on the entropy change for these reactions in hydrocarbon media, those values reported by Smith for $^i\text{Bu}_3\text{Al}$ ($\Delta S = 128(1) \text{ J mol}^{-1} \text{K}^{-1}$), Et_3Al (135(3)) and that estimated for Me_3Al (122(1)) compared with gas phase values of 177(2) and 190(3) for Me_3Al and Et_3Al , or theoretical estimates (*vide infra*) appear reasonable. The much lower values reported by Černý and co-workers (entries 4–5 and 6–7) do not, and suggest an

Table 2 Experimental data for dissociation of R_6Al_2 in condensed phase^a

Entry	R	ΔT (°C)	ΔH	ΔS	ΔG^b	ΔG^c	Solvent	Ref.
1	^iBu	10–45	34.1(5)	128(1)	−3.92(4)	—	^d	27
2	Et	60–150	71(1)	135(3)	—	30.5(6)	^d	25
3	Et	60–150	55.7(5)	100(2)	—	25.9(5)	^e	28
4	Et	60–100	44(5)	69(26)	23(0)	23(9)	^f	29a
5	Et	60–100	40(2)	65(12)	20(7)	20(4)	^g	29a
6	Me	40–100	54(2)	74(6)	32(2)	32(3)	^f	29b
7	Me	40–100	55(6)	81(16)	30(5)	31(6)	^e	29b
8	Me	—	81(1)	122(1)	—	45(1)	^d	25
9	Me	—	63.8(4)	—	—	—	^e	28

^a ΔG and ΔH in kJ mol^{-1} , ΔS in $\text{J mol}^{-1} \text{K}^{-1}$ with estimated standard deviation in parentheses. ^b Estimated from data obtained at 298 K.

^c Extrapolated from data at higher T to 298 K. ^d Liquid or hydrocarbon solution. ^e Mesitylene. ^f Heptane. ^g Xylenes.



insufficiently large temperature range was used or other sources of error are involved. Certainly, the error in some reported values for ΔS is unacceptably large (e.g. entries 4 and 7).

On the other hand, in the case of Me_3Al , $\Delta G = 45(1) \text{ kJ mol}^{-1}$ at 298 K extrapolated by Smith corresponds to an equilibrium constant of $1.3 \times 10^{-8} \text{ M}$ in hydrocarbon solution. Based on the work of Černý *et al.* no change in ^{27}Al chemical shift would be expected over the concentration range they studied, while the measured equilibrium constant is $3.1(1.6) \times 10^{-6} \text{ M}$, admittedly with a large error involved.

Concerning calculations, approximating solution Gibbs energy for dissociation of Me_6Al_2 by the $\frac{2}{3}\text{TS}$ scaling factor¹⁷ leads to good agreement ($\Delta G\text{-c} = 28.8 \text{ kJ mol}^{-1}$) seen in the more recent experimental work (Table 2, entries 6 or 7). However, this approach has limited applicability for large systems, where the total entropy is dominated by vibrations, whilst translations are primarily affected when moving from gas-phase to solution.

The thermodynamic functions calculated for dissociation of R_6Al_2 by polarizable continuum method (PCM)³⁰ in a variety of media are given in the ESI (Table S-1†). Though a slight decrease is predicted for ΔH or $\Delta H\text{-qh}$ relative to gas phase, we do not reproduce the much lower values seen experimentally. To account for specific solvation of reactants and products, we looked at solvent–solute interactions, subtracting the difference in $\Delta H\text{-qh}$ between R_3Al -solvent and R_6Al_2 -solvent interactions ($\Delta\Delta H$ in Table 3) from the PCM results for the thermodynamic functions. The lower reaction enthalpies seen in both hydrocarbon and especially in aromatic hydrocarbon solution are related to this phenomenon.

The final data are summarized in Table 3, and Fig. 2 illustrates the molecular structures of the R_6Al_2 dimers in both gas-phase and under specific interactions with two heptane molecules, one for each half of the dimer.

If we focus on the data for Et_3Al , the theoretical estimates of $\Delta H\text{-qh}$ in mesitylene (55.3 kJ mol^{-1}), heptane (72.0) or for $\text{i-Bu}_3\text{Al}$ in heptane (37.5) are within a few kJ mol^{-1} of the corresponding experimental values reported by Smith (Table 2, entries 1–3). We cannot confirm the experimental findings of Černý and coworkers, who reported much lower values for the enthalpy changes for Et_3Al (and Me_3Al) and quite similar

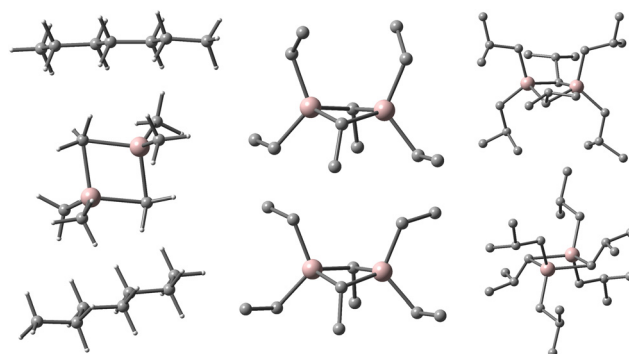


Fig. 2 The preferred conformations of Et_6Al_2 (middle) and $\text{i-Bu}_6\text{Al}_2$ (right) in gas-phase (bottom) and when interacting with two heptane molecules (top) as illustrated for Me_6Al_2 (left). Al in pink, C in grey, H omitted for clarity for Et_6Al_2 and $\text{i-Bu}_6\text{Al}_2$.

values in hydrocarbon and aromatic hydrocarbon solution. As will be shown below, the interaction energies between Me_3Al and itself or other molecules at the M062-X/TZVP level of theory are accurate within 4–5 kJ mol^{-1} of the values obtained by the CCSD(T) method.

The experimental values provided by Černý and coworkers lie well outside this limit of theoretical error. We conclude that our theoretical estimates for $\Delta H\text{-qh}$ for Me_3Al in both solvents (Table 3, entries 1 and 2) should be considered reliable. While the value in mesitylene (60.5 kJ mol^{-1}) is in reasonable agreement with Smith's estimate (63.8 kJ mol^{-1}), our theoretical estimate in hydrocarbon (71.4 kJ mol^{-1}) is significantly lower than Smith's (81 kJ mol^{-1}). This may account for his estimate for K_d and ΔG at 298 K being inconsistent with the measurements of Černý and coworkers at that temperature.

Alignment of theory vs. experiment cannot rely solely on accurate estimation of ΔH and thus ΔS requires attention. The PCM model as such cannot account for the observed reduced entropy in solution, as is clear from the calculated $\Delta S\text{-qh} \approx 188 \text{ J mol}^{-1} \text{ K}^{-1}$ for Me_6Al_2 dissociation at $T = 298\text{K}$ in both gas-phase (Table 1, entry 4) and in any of the solvents (Table 3), while the range of the measured entropies is lower, 74–122 $\text{J mol}^{-1} \text{ K}^{-1}$ (Table 2). Therefore, to account for the restricted movements in solution, the entropies determined in continuum were corrected for the reduced accessible space

Table 3 Theoretical thermodynamic data for dissociation of R_6Al_2 in condensed phase^a

R	Solvent	ΔH	$\Delta H\text{-qh}$	$\Delta\Delta H^b$	ΔG (ΔS)	$\Delta G\text{-qh}$ ($\Delta S\text{-qh}$)	$\Delta G\text{-qh-tr}^c$ ($\Delta S\text{-qh-tr}$)
Me	Mesitylene	58.3	60.5	19.1	−9.5 (228)	4.6 (188)	18.6 (141)
Me	Heptane	70.9	71.4	7.8	−6.3 (259)	15.1 (189)	27.9 (146)
Me	Benzene ^d	63.2	63.5	14.6	−7.7 (227)	4.6 (188)	19.2 (142)
Et^e	Mesitylene	59.1	55.3	22.3	−28.5 (264)	−12.9 (229)	1.1 (182)
Et^e	Heptane	73.3	72.0	6.5	−9.2 (276)	4.2 (228)	17.0 (184)
i-Bu^f	Heptane	36.9	37.5	0.2	−31.9 (231)	−35.8 (246)	−23.0 (203)

^a ΔG and ΔH in kJ mol^{-1} , ΔS in $\text{J mol}^{-1} \text{ K}^{-1}$. Additional data are reported as ESI.† ^b Difference in $\Delta H\text{-qh}$ due to specific solvation of reactant vs. product, calculated as the difference between $\Delta H\text{-qh}$ in R_3Al -solvent and R_6Al_2 -solvent interactions. ^c Corrected for both low energy vibrations and reduced translational entropy in solution. See text for discussion. ^d 313 K cf. Table 5. ^e C_2 symmetry adopted in solution in the presence of specific Et_6Al_2 -solute interactions; C_s symmetry in gas phase (see Fig. 2). ^f C_2 symmetry in solution; gas-phase C_i symmetry (see Fig. 2).



due to the volume occupied by the solvent, resulting in reduced translational entropy, as describes by Whitesides and co-workers.¹⁹

The translational entropy correction (tr) combined with the harmonic entropy correction (qh) provides our best estimates of the free energy change, labeled ΔG -qh-tr in Table 3. These combined corrections take us towards the experimentally measured entropies (Table 2). Still, the ΔG -qh-tr values are not in quantitative agreement with experiment though we predict the ease of dissociation correctly (Me < Et << i-Bu) and in the different solvents (*i.e.* more dissociated in aromatic hydrocarbon due to lower ΔH).

There are several potential reasons for the remaining discrepancy in ΔS between theory and experiment. The experimental values suggest that motion is more restricted in solution than indicated by the approximation in use. The approximation based on free volume indicates an entropy lowering of ΔS -qh-tr – ΔS -qh = $\Delta\Delta S = 43$ – 47 J mol^{−1} K^{−1} for the various solvents at 298 K. We note that another approximation based on the increased density and thus pressure of the liquid state^{16c} leads to $\Delta\Delta S$ values of almost identical magnitude. If we were to further restrict translation using densities typical for organic glasses (*ca.* 1300 kg m^{−3}) we estimate $\Delta\Delta S = 46$ – 50 J mol^{−1} K^{−1} suggesting either approach has limits of this magnitude.

Neither approximation leads to limiting values of ΔS -qh-tr that match experiment. It is possible that rotations are also constrained in the liquid state but the rotational entropy (S -r) of the products (2×99.7 J mol^{−1} K^{−1} in the case of Me₃Al) might be expected to decrease in proportion to that of the reactant (119.1 J mol^{−1} K^{−1}), where the difference is ΔS -r = 80.3 J mol^{−1} K^{−1} in gas phase at 298 K. A reduction similar to that seen for translations, which we don't think is justified here,³¹ would lead to a further lowering of perhaps no more than 20 J mol^{−1} K^{−1}. This would bring us into quantitative agreement with the results of Smith in hydrocarbon media.

Besides being systematically higher, the calculated entropies (for R = Me, ΔS -qh-tr = 141 or 146 J mol^{−1} K^{−1} in aromatic or aliphatic hydrocarbon solution) are insignificantly different in the two different media compared to experiment (*cf.* Table 2, entries 2 and 3). We suspect this also reflects that both products and reactants are specifically solvated, which would have the effect of reducing the entropy further and may account for the significant difference between aromatic *vs.* aliphatic solvents seen experimentally but not theoretically.

We end this section with a discussion of the energetic consequences of specific solvation as studied using the M06-2X and MN15³² functionals, def2-TZVP³³ and def2-TZVPD³⁴ basis sets and CCSD(T) method. The data are summarized in Table 4.

The first entry corresponds to the energy change for dimerization of Me₃Al, which can be thought of as an interaction energy as Me₆Al₂ is energetically the most stable adduct of Me₃Al with itself. The single-point CCSD(T)/def2-TZVPD energies calculated for the MP2/def2-TZVPD optimized geometries provide an instructive reference. At this sophisticated level of theory, the Me₃Al dimerization energy is calculated as -96.5 kJ

Table 4 Interaction energies ΔE (kJ mol^{−1}) of Me₃Al and Me₆Al₂ adducts

Adduct	M06-2X ^a	M06-2X ^b	MN15 ^b	MN15 ^c	CCSD(T) ^d
Me ₃ Al-AlMe ₃	−92.1	−98.2	−103.7	−104.5	−96.5
Me ₃ Al-C ₇ H ₁₆	−23.8	−23.8	−33.0	−34.2	−25.7
Me ₃ Al-C ₆ H ₅ CH ₃	−40.5	−40.8	−48.8	−49.3	−43.4
Me ₃ Al-C ₆ H ₃ (CH ₃) ₃	−48.2	−48.1	−58.0	−58.6	−51.4
Me ₃ Al-C ₆ H ₆	−36.1	−36.6	−44.0	−44.4	−39.0
Me ₆ Al ₂ -C ₆ H ₆	−19.7	−19.5	−25.1	−25.5	−25.4

^a TZVP. ^b def2-TZVP.³³ ^c def2-TZVPD.³⁴ ^d CCSD(T)/def2-TZVPD single-point energy in MP2/def2-TZVPD optimized geometry.

mol^{−1}, which when combined with the quasi-harmonic enthalpy correction calculated at MP2/def2-TZVPD level of theory, gives ΔH -qh = -84.2 kJ mol^{−1}, *i.e.* in precise match with the experimental enthalpy of 84.2 kJ mol^{−1} for the reverse reaction, quoted from Table 1.

Our method of choice, M06-2X/TZVP underestimates the Me₃Al dimerization energy by *ca.* 4 kJ mol^{−1} (which we already saw in the discussion of Me₃Al dissociation enthalpies, Table 1). While improving the basis set to def2-TZVP might be justified, it has very little effect on the solvent interactions (Table 4, second column), based on which, the effect of specific solvation on dissociation was calculated (Table 3). As for dimerization of Me₃Al, M06-2X is more accurate than MN15, which is consistent with previous evaluations of X₃Al dimerization energies in general.³⁵ However, when it comes to noncovalent interactions, MN15 is better suited to describe those as the Me₆Al₂-benzene interaction energies are very closely aligned to the CCSD(T) results.

If we consider the specific case of dissociation of Me₆Al₂ in benzene, the dissociation energy is within 4.4 kJ mol^{−1} of the theoretical limiting value, while we underestimate solvation of the Me₃Al product by 2.9 kJ mol^{−1} and of Me₆Al₂ by 5.7 kJ mol^{−1} with respect to the CCSD(T) results. So, overall, our M06-2X/TZVP results are about 7.2 kJ mol^{−1} lower in electronic energy for this reaction than predicted at the CCSD(T) level of theory. This provides some indication of the errors involved when it comes to equilibria involved in larger systems featuring non-covalent interactions, as in the section dealing with metallocenium ion pairs (*vide infra*).

Dissociation of R₆Al₂ *vs.* kinetics of alkyl exchange

The continuing study of the dissociation equilibrium has been motivated by kinetic work focused on the mechanism of exchange of bridging and terminal Al-R groups in these compounds,³⁶ which can be studied by dynamic NMR spectroscopy. There is consensus from this work that the enthalpy of activation decreases in the order Me > Et > higher alkyls and the exchange process is significantly faster in aromatic *vs.* aliphatic media at the same temperature.³⁷ Accepted values for $\Delta H^\ddagger$ vary between 63–67 kJ mol^{−1} for R = Me in hydrocarbon media between 263 and 213 K with $\Delta G^\ddagger = 46.0$ kJ mol^{−1} at 223 K. An early study featuring the widest temperature range



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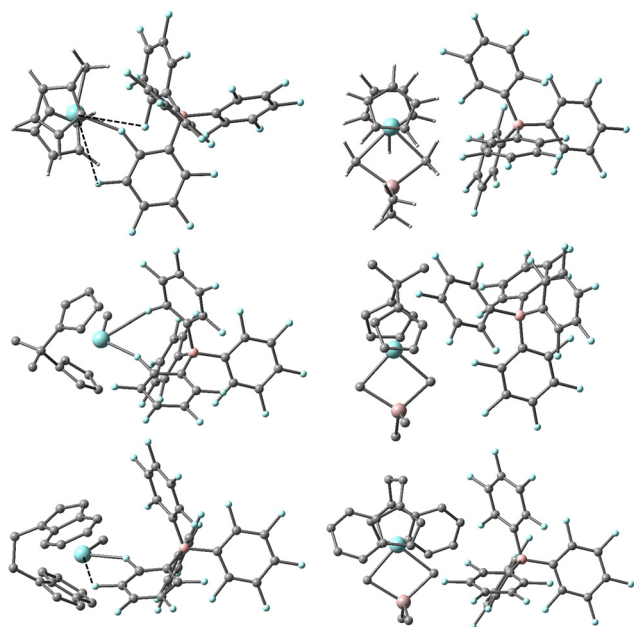
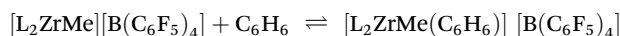


Fig. 3 Most stable structures of $[\text{L}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{L}_2 = \text{Cp}_2$,⁴⁵ Me_2CCp_2 and EBI , left) and $[\text{L}_2\text{ZrMe}_2\text{AlMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (right) based on Gibbs energy ($\Delta G\text{-qh-tr}$) at the M062-X/TZVP level of theory. Zr and F in blue, Al and B in pink, C in grey, H omitted from lower two structures for clarity. Long Zr–F contacts are shown as dashed lines.

system is intermediate between these extremes with one short ($\text{Zr-}o\text{-F} = 2.335 \text{ \AA}$) and one longer ($\text{Zr-}m\text{-F} = 3.117 \text{ \AA}$) contact involving the same C_6F_5 ring. We should note that similar structures have been detected in simulations involving $[\text{Me}_2\text{SiCp}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ at a lower level of theory.⁴⁰ We suspect these different interactions between anion and cation lead to the larger spread in free energy differences for the different ligands, while the experimental results suggest the involvement of species in which the effect of the anion has been mitigated to some extent.

We thus considered specific solvation of reactant *vs.* product ion-pairs by benzene. We found that both the Zr cation and the anion were susceptible to specific solvation, though inclusion of two benzene moieties led to results that were not significantly different compared to just one (Table 5, entry 7 *vs.* 8). In some CIP structures the coordinated benzene was also involved in arene-perfluoroarene interactions with the anion⁴⁸ (see ESI,[†] *e.g.* $[\text{Cp}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ -benzene isomer 2). Inclusion of specific solvation has the desired effect as we move closer to experiment in all three cases, where the differences now result in K_d values that differ by less than 160 at 313 K. We should temper this positive result by stating that binding of benzene to the thermodynamically most stable CIP (and also OSIP) is endergonic with $\Delta G\text{-qh-tr} = 6.7$ to 16.1 kJ mol^{-1} for the equilibrium:



However, since we underestimate the $\text{Me}_2\text{Al}_2\text{-C}_6\text{H}_6$ interaction energy at the M06-2X/TZVP level of theory by 5.7 kJ mol^{-1} (Table 4), it is probable that we underestimate enthalpy

changes at least by the same amount for equilibria of this type. We hesitate to apply any quantitative correction and conclude that specific solvation is undoubtedly important.

Dissociation of $[(\text{L}_2\text{ZrMe})_2\text{Me}]^+$

Our third and final test equilibrium is dissociation of $\text{Cp}''_2\text{ZrMe}_2$ from $[(\text{Cp}''_2\text{ZrMe})_2\mu\text{-Me}][\text{MePBB}]$ ($\text{Cp}'' = 1,2\text{-Me}_2\text{C}_5\text{H}_3$, $\text{PBB} = \text{tris-(perfluorobiphenyl)borane}$) in toluene.⁴⁹ This dinuclear ion-pair was fully characterized in solution and the solid state. The dinuclear cation features an *s-gauche* geometry¹⁵ with a dihedral angle $\text{Me-Zr}\cdots\text{Zr-Me}$ angle $\varphi = 108.5^\circ$ and a near linear geometry for the $\mu\text{-Me}$ bridge ($\angle\text{ZrMeZr} = 170.9^\circ$). However, we find in the presence of the counter-anion in gas phase and toluene continuum that a *syn* isomer with $\angle\text{ZrMeZr} = 171.0^\circ$ and $\varphi = 37.7^\circ$ (Fig. 4) is most stable electronically, compared to two *anti* stereoisomers with $\Delta E = 7.4$ and 9.0 kJ mol^{-1} . The higher energy of these corresponded to the X-ray structure.

In comparing the two structures, it is obvious that the theoretical structure has a much closer contact of the anion with the cation, as would be expected for an isolated ion-pair in gas or condensed phase in a low dielectric medium.

In earlier work, several limiting conformers were located for dinuclear cations of this type with the stability of the *syn* isomers ($\varphi < 90^\circ$) *vs.* the *anti* conformers ($\varphi > 90^\circ$) being dependent on ligand structure in gas phase.^{15,50} Thus, the X-ray structure more closely resembles the situation in gas or condensed phase of an isolated cation, while our DFT results suggest that close contact of anion and cation induces a conformational change in the latter.

In discussing the dissociation equilibrium we considered three *anti* and *syn* $[(\text{Cp}''_2\text{ZrMe})_2\mu\text{-Me}][\text{MePBB}]$ stereoisomers located by theory. The results are summarized in Table 6.

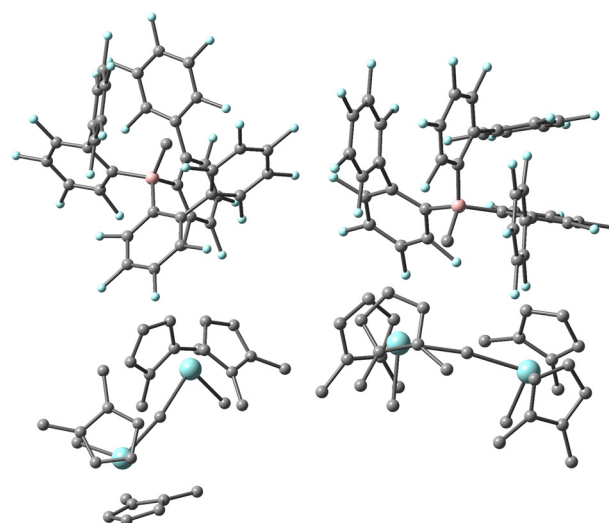


Fig. 4 X-ray structure of $[(\text{Cp}''_2\text{ZrMe})_2\mu\text{-Me}][\text{MePBB}]$ ($\text{Cp}'' = 1,2\text{-Me}_2\text{C}_5\text{H}_3$, $\text{PBB} = \text{tris-(perfluorobiphenyl)borane}$) (left) and thermodynamically most stable structure (right) located by DFT. Zr and F in blue, B in pink, C in grey, H omitted for clarity.



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tion with the TZVP basis set.⁸ Interaction energies summarized in Table 4 employed in addition the MN15 density functional³² in combination with a def2-TZVP³³ or def2-TZVPD³⁴ basis set, and frozen-core CCSD(T)/def2-TZVPD single point calculations carried out at MP2/def2-TZVPD optimized geometries. Relativistic effective core potential of 28 electrons was used to describe the core electrons of Zr.⁵⁵ Polarizable continuum model calculations were employed by the integral equation formalism variant (IEFPCM).³⁰ We also tested the SMD variation of IEFPCM,⁵¹ with similar results, but decided to abandon it due to significant convergence issues. Stationary points were confirmed as minima by harmonic vibrational frequency calculations. All calculations were carried out using Gaussian 16.⁵²

Quasi-harmonic corrections to the entropy¹⁴ and enthalpy²³ were employed using cut-off frequency of 100 cm⁻¹ and corrections to reduced translational entropy in solution were calculated by the method described by Whitesides *et al.*¹⁹ All the corrections were employed using the Goodvibes script,⁵³ modified to include molarities and molecular volumes of the solvents, which were required for calculation of free accessible space.⁵⁴

Author contributions

M. L. carried out the quantum chemical calculations. M. L. and S. C. jointly aligned theory with experiments and co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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